

THE IDENTIFICATION OF CERTAIN CLAYS
BY DIFFERENTIAL THERMAL ANALYSIS

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THE IDENTIFICATION OF CERTAIN CLAYS

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DIFFERENTIAL THERMAL ANALYSIS

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PREFACE

It is the purpose of this investigation to ascertain the effect of certain variable conditions - heating rate, mineral grain size, etc. - on the differential thermal curves of three clay minerals - Kaolinite, Bentonite, and Illite - and to prepare standard characteristic thermal curves for these clay minerals. It is further desired to develop a method of quantitative analysis of clays containing these minerals using these standard thermal curves.

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INTRODUCTION

In working with clays and soils, great difficulty is encountered in identifying the minerals in the finer fractions. The petrographic method is satisfactory for the larger grain size range; X-ray diffraction is good for the finer grains when they occur in fairly large proportions; chemical analysis - time consuming and expensive - results in an accurate quantitative analysis but fails to indicate the manner in which the constituents are combined in the clay mineral. For over 60 years, differential thermal analysis has been used for the identification of clay minerals, and since 1938 (6) several investigators have proposed methods by which the differential thermal curve may be adapted to quantitative analysis. In brief, this analysis consists of heating at a constant rate a small quantity of a material to 1000°C, or as close to fusion as experimentally possible, and recording, by suitable apparatus, the endothermic and exothermic reactions that occur in the substance. All investigations indicate that the differential thermal method is particularly suited to the identification of clay minerals when they occur in grain sizes finer than the limits of the petrographic method, or when they occur in mixtures in which the X-ray diffraction method is not practicable. A differential thermal test can be conducted much more

quickly and economically than the chemical analysis and with proper interpretation of the thermal curve more definite information as to the clay structure is possible.

The value of the differential thermal method, first suggested in 1887 by M. H. LeChatelier, was not realized until 1935 when J. Orcel (7) presented a paper giving thermal curves for most of the clay minerals and many natural clays. Although Orcel suggested a possibility of quantitative measurement, no such analysis was attempted until 1938 when Norton published his results (6). Further studies of this method have since been made by several investigators, notably Grim (1,2), Insley and Ewell (4), Page (8), and Hendricks, et al (3). The results of the several investigators are not comparable, possibly because of variations in experimental procedure. For example: preheat conditions might effect the thermal curve - Norton and Page used air dried while Grim and Rowland preheated their samples twelve hours at 90°C.; or the rate of heating might have an effect - LeChatelier heated his samples 120°C. per minute, Norton used 12° per minute, and Page used 8.2° per minute; or again the grain size of material tested might account for variations in results - Norton used material passing a 150 mesh sieve, Page used material passing an 80 mesh sieve, Bystrowski (R.P.I. 1949) passed his samples

through a 60 mesh sieve. Other factors - quantity of material, packing of sample, position of thermocouples, etc. - could be causes of the incomparable thermal curves. However, all investigators agree as to the type and temperature range for the thermal reactions of a given mineral.

Deflections in the differential thermal curve of a mineral represent energy changes, involving either molecular rearrangement or dehydration (loss of either adsorbed water or lattice OH-ions). When a substance undergoes molecular rearrangement, it would naturally change to a more stable system, thereby liberating energy, and thus appear as an exothermic reaction on the thermal curve. On the other hand, the dehydration of a system requires additional energy and would show as an endothermic reaction.

For the three clay minerals we are investigating, the general thermal characteristics are as follows:

KAOLINITES. The thermal curve exhibits an endothermic reaction at 550-600°C. and an abrupt intense exothermic reaction at 950-1000°C. Most investigators agree that the endothermic reaction accompanies the dehydration of the mineral and the exothermic reaction is associated with the formation of gamma-aluminum oxide.

ILLITES. The thermal curves show endothermic peaks at 100-200°C., 500-650°C., and about 900°C., and an exothermic peak immediately following the third endo-

thermic peak. The first endothermic peak indicates the loss of swelling water (water held between the basal planes of the lattice structure), the second endothermic peak accompanies the loss of most of the lattice water; and the third endothermic peak is associated with the final destruction of the illite structures. The exothermic peak is probably associated with the formation of spinel.

MONTMORILLONITES. The thermal curves show endothermic peaks at 150-200°C., 600-700°C., and 800-900°C., and an exothermic peak immediately following the last endothermic peak. The initial endothermic peak, as in the curves for illites, represents the loss of swelling water; the second endothermic peak accompanies a loss of lattice water. The reason for the third endothermic peak is not fully agreed upon by all investigators - Grim and Rowland (2) suggest that it is associated with lattice disruption, whereas Page (8) maintains that it is due solely to the loss of the remaining lattice water. The exothermic peak probably accompanies the formation of spinel.

The kaolinite and illites both have an endothermic reaction between 500 and 600°C. However, the intensity of the kaolinite reaction is about ten times that of the illite. This can be partially explained by the fact that the 1:1 lattice clay mineral (kaolinite) loses more water

than the 2:1 lattice clay mineral (illite); further, Grim and Rowland suggest that this reaction also represents the destruction of the 1:1 lattice. The kaolinite curves are more regular and show less variation than the illite curves. It has not been satisfactorily explained why the second endothermic peak occurs 100°C. higher in montmorillonites than in illites, when both clay minerals have the 2:1 lattice and about the same amount of lattice water. The third endothermic peak appears to be characteristic of 2:1 lattice clay minerals.

EQUIPMENT AND EQUIPMENT CALIBRATION

EQUIPMENT

The equipment used in the differential thermal analysis is the same as that used in investigations by F. P. Bystrowski in June 1949, with the addition of a Brown Recording Potentiometer Pyrometer which records furnace temperature and automatically regulates the heating rate.

The test furnace is a heavy duty, combustion type - Hoskins Model FH-305 - 12 inches long and with an inside diameter of 2 1/32 inches. The furnace is supplied by a transformer rated at one kilowatt which at maximum input (20 volts and 50 amperes) will heat the furnace to 1100°C in approximately 30 minutes.

The specimen holder, developed by J. E. Munzer, is a nickel block with two sample wells (volume approximately 1.15 cc. each) one well for the test sample, the other for the thermal standard. In each of these wells, there is a temperature measuring thermocouple, and a differential temperature thermocouple is placed across the wells. All thermocouples were made from Brown and Sharpe 18 gage chromel and alumel wire stock. It might be well to point out that the differential temperature thermocouple consists of two leads of chromel wire bridged by a short length of alumel wire - the junctions of these dissimilar metals being approximately centered

in the sample wells. Connection of furnace thermocouples to the automatic recording equipment is made through a Jones Plug, which permits the operation of several furnaces with one set of relatively expensive recording equipment.

To facilitate the collection of data, autographic recording equipment is employed. A Speedomax - Type 6, Model S-60,000 Series, Leeds and Northrup Recorder, capable of recording temperatures from 0 to 1200 degrees centigrade and differential temperatures ranging between plus and minus 1.5 millivolt equivalents - measures the temperature of the clay sample and the difference in temperature between the clay sample and the thermal standard. This multiple point recording apparatus, when operated as a two point recorder, plots thermal curves directly, successive points on each curve being printed every six seconds. Inasmuch as thermal curves are printed on paper calibrated in degrees centigrade, the temperature of the test sample may be read directly from the record sheet; whereas the evaluation of the differential thermal curve requires the superimposition of an equivalent millivolt scale.

An autographic Brown Potentiometer Pyrometer, with a temperature range of 0-1200 degrees centigrade, is used to record the temperature of the thermal standard and to control the rate of increase in furnace temperature. The thermal standard temperature is printed continuously

on paper graduated in degrees centigrade allowing direct measurement. A motor driven variable transformer (Variac V-20), with a rated output of 3.45 kilowatts and operating between 0 and 135 volts, is placed in series between the power source and the furnace transformer thereby controlling the voltage input to the furnace. The output of the Variac is controlled by the Brown Pyrometer which is mechanically adjusted to maintain the desired rate of temperature increase.

An Elconap Oven Model DPC-M-60292, is used to preheat the materials tested. For sample fractionation we use a Cenco-Meinzer Sieve Shaker, Cat. No. 18480. Thermocouple calibrations are made in a Hevi-Duty Multiple Unit Electric Muffle Furnace, Type 66-F, with a maximum temperature of 1000 degrees Centigrade.

EQUIPMENT CALIBRATION

THERMOCOUPLES: - All temperature measuring thermocouples are calibrated according to the following procedure: (1) An 8 gage chromel-alumel thermocouple -calibrated by measuring its millivolt equivalent output at known temperatures. (in this case, check temperatures selected were the freezing and boiling points of distilled water and the freezing points of chemically pure lead and aluminum) - is used as a standard; (2) each thermocouple used

in the thermal tests is calibrated by comparing its millivolt equivalent output against that of the standard when they are heated together in the muffle furnace. All thermocouples so tested were in very close agreement with standard chromel-alumel millivolt equivalents, for which the recording equipment is calibrated, that correction of the thermal curves for such variation is not necessary. Thermal tests were conducted from 0 to 1000 degrees centigrade with the thermal standard (calcined alumina) in both sample wells, with the intention of correcting the differential thermal curve for any temperature differences recorded. No such corrections were found necessary.

RECORDING EQUIPMENT: Both autographic recorders are equipped with compensators which automatically correct the millivolt equivalent inputs from the temperature measuring thermocouples for variations in machine cold junction temperature; i.e., the temperature curves printed should show actual temperature of the materials in the specimen holder. However, with our wiring arrangement, additional cold junctions are in the circuit between the furnace thermocouples and the recording equipment which might affect the value of temperatures printed. To evaluate this effect, we immersed the specimen holder in boiling distilled water while the recording machines were in operation and noted the external

cold junction temperature. The difference between the printed temperatures and 100 degrees centigrade is a constant correction which should be applied to the thermal curves (which are run at the same external cold junction temperature) to obtain the actual temperatures of the materials in the specimen holder.

PROCEDURE

A differential thermal curve, a measure of energy changes in a substance during heating, is a graphical representation of the lead or lag of the sample temperature with respect to that of a thermal standard throughout the test temperature range. This curve is plotted with the temperature of the thermal standard as abscissa, the ordinate being the temperature difference between the test material and the thermal standard expressed in millivolt equivalents of the thermocouple used.

The curves of previous investigators are not comparable; some possible reasons for this have been mentioned in the Introduction. To the best of our knowledge we have analyzed all factors which might possibly effect a thermal curve - our consideration of these factors will now be discussed.

Obviously, the differential thermal curve depends primarily upon the material tested. As heretofore stated, we are testing materials which are representative of the three types of clay minerals - for the kaolinitic type, lumps of kaolinite from Georgia (Ward's Natural Science Establishment, Inc.); for the Montmorillonitic type, Volclay Wyoming Bentonite (American Colloid Company); and for the Illitic type, Illite-purified from shale - from

Fithian, Illinois (Ward's Natural Science Est., Inc.).

The energy change of a mineral, represented in the differential thermal curve as the area under a peak, is directly proportional to the amount of material heated. The volume of material tested is limited by the size of the test well in the sample holder; the amount of material in the well can be controlled easily by using a definite packing procedure. By subjecting all materials tested (including the thermal standard) to uniform preheat conditions, the free water content of the samples, which would effect the initial portion of the curve, can be controlled. Theoretically, variations in atmospheric pressure could change slightly the temperatures at which endothermic reactions occur; however, for the purpose of this investigation, such an effect is considered negligible. Variations in atmospheric temperature, which directly effect the thermocouple cold junctions and, therefore, indirectly effect the temperatures recorded, can be compensated for as previously mentioned in the section on recording equipment calibration. The type of thermocouple used and its location within the sample are other factors which can be controlled; in our sample holder, the chromel-alumel thermocouples are fixed in place in the sample wells. Many investigators have noted variations in the curve of a mineral when different

rates of heating are used. We believe that variation in the grain size of a clay mineral, and possibly that of the thermal standard, might also effect the differential thermal curve.

As shown above, the effect on a curve of all factors considered, with the exception of the heating rate, and the grain size of the clay mineral and thermal standard, can be eliminated, compensated for, or controlled by the proper selection of apparatus and testing procedure. The effect of any one of the excepted factors can be studied by varying it through a desired range while the other factors are held constant.

The purpose of this investigation is to establish standard differential thermal curves for three clay minerals - Kaolinite, Bentonite, and Illite - and to develop a method, using these curves, for analyzing quantitatively mixtures of these minerals. We propose to accomplish this by: (1) conducting a series of tests at varying heating rates, all other variables being controlled, and selecting a rate, which results in good working curves, to be used in all later tests; (2) studying the effect of variation in the grain size of the thermal standard and the clay minerals; (3) establishing the standard thermal curves; (4) testing prepared mixtures and deriving from the resulting curves a method of quantitative analysis.

ADOPTED TEST PROCEDURE

To maintain uniform test conditions and obtain reproducible curves the following test procedure is used:

1. All material is ground (if necessary) and fractionated. The four grain size ranges investigated were: 60-100; 100-140; 140-200; and 200-Pan, (Figures used are U. S. Standard Sieve Numbers.)
2. All material is preheated at 50°C for at least 24 hours.
3. The material is resieved immediately prior to testing.
4. Both the test material and the thermal standard are tapped to maximum consolidation in their respective sample wells and the loaded specimen holder is then placed in the furnace.
5. The Brown Recording Potentiometer Pyrometer is now mechanically balanced, turned off, and the heating rate control indicator (Black) and the thermal standard temperature indicator (Red) are both set at 50°C.
6. The Speedomax is placed in operation, balanced, and allowed to reach equilibrium. Since the compensating device (for machine cold junction temperature) for this

recorder is not separately enclosed,
the access door must remain closed
during the test period - this includes
time which the machine requires to
reach equilibrium.

7. The furnace is turned on and the actual test is started.
8. When the speedomax records a sample temperature of 50°C, the Brown Recorder is placed in operation.
9. External cold junction temperatures are recorded.
10. When the sample temperature is slightly above 1000°C, the automatic cutoff switch on the Brown Recorder turns off all equipment, thereby completing the test.

Step (3) in the above procedure might not at first appear necessary. However, we find that Kaolinite after being preheated partially breaks down into finer fractions. This is not true of the illite and bentonite.

When prepared mixtures are to be tested, the above procedure may be used with the following modification of steps (3) and (4).

3. (a) All material is resieved after being preheated.

- (b) The desired mixture is prepared from

requisite volumes (tapped to maximum consolidation). The mixture is made in quantity sufficient for at least three tests.

4. (a) Both the test material and the thermal standard are tapped to maximum consolidation in their respective sample wells and the loaded specimen holder is then placed in the furnace. The remaining quantity of the mixture is returned to the preheat oven.
- (b) In further tests, the mixture is placed in the specimen holder directly from the preheat oven - the mixture is not resieved.

RESULTS AND CONCLUSIONS

Each of the appended differential thermal curves is the average of several tests (usually three). The maximum variation in peak temperature is 10°C (for the large Kaolinite endothermic reaction); the average maximum variation is 2.5°C . The maximum variation of any peak intensity is .08 millivolts (occurring at the large Kaolinite endothermic reaction); the average maximum variation is 0.018 millivolts.

EFFECT OF VARIATION IN HEATING RATE ON THE DIFFERENTIAL THERMAL CURVE OF KAOLINITE (See Appendix C)

This effect can be studied, as explained on page 13, by controlling all other variable factors -- the grain size of the clay mineral (Kaolinite) and the thermal standard is held constant (at 100-140) -- and conducting tests over a wide range of heating rates. At least two tests were made at each of eight heating rates varying from 598°C to $1352^{\circ}\text{C}/\text{Hr.}$ It is evident from appended curve C-1 that the intensity of the endothermic peak varies directly with the heating rate, i.e., the peak intensity increases with increasing heating rate.

A heating rate of $1023^{\circ}\text{C}/\text{Hr.}$, which resulted in a good working curve, is used in all further investigations.

EFFECT OF VARIATION IN THERMAL STANDARD GRAIN SIZE ON THE DIFFERENTIAL THERMAL CURVES

This effect was studied in two ways: (1) with 60 mesh calcined alumina as the thermal standard, calcined alumina of various grain sizes - ranging from 60 mesh through a 200 mesh sieve - was used as the test material; (2) with each of the four grain sizes of Kaolinite as the test material, calcined alumina - of both 60 mesh and the grain size corresponding to that of the test material - was used as the thermal standard. The differential thermal curves from the first series of tests were straight lines at zero millivolts; in the second series of tests, the variation in the thermal standard grain size did not change the differential thermal curves. Therefore, it was concluded that the effect of the variation of the thermal standard grain size, through the range tested, on the differential thermal curves was negligible. However, for continuity in all remaining tests, the grain size of the thermal standard was the same as that of the test material.

EFFECT OF VARIATION IN THE CLAY MINERAL GRAIN SIZE ON THE DIFFERENTIAL THERMAL CURVES (See Appendix D)

To study this effect, at least three tests were made on each of the four grain sizes (60-100, 100-140, 140-200, 200-Pan) of the clay minerals -- Kaolinite, Bentonite and Illite.

KAOLINITE: As shown on appended curve D-1-a, the intensity of the endothermic reaction at approximately 600°C diminishes with decreasing grain size, and the displacement of that portion of the curve beyond this reaction increases in the positive (exothermic) direction with decreasing grain size. The exothermic reaction at approximately 1000°C is so abrupt and intense that our recording equipment cannot record accurately the peak ordinate; therefore, this reaction can be used only for qualitative analyses. The decrease in the endothermic peak intensity with decreasing grain size is emphasized by appended curve D-1-b. This can be readily explained by the fact that, with the finer grain sizes, less material can be packed into a given volume; thus, the finer fractions absorb less heat.

BENTONITE: As shown on appended curve D-2-a, the intensity of the second and third endothermic peaks (approximately 720°C and 920°C, respectively) increase with decreasing grain size, the exothermic peak (approximately 960°C) decreases with decreasing grain size, and the displacement of that portion of the curve beyond the second endothermic reaction increases in the negative (endothermic) direction with decreasing grain size. The first endothermic peak (approximately 160°C) represents the loss of

swelling water - a variable quantity - and cannot be used for either qualitative or quantitative analyses. The change in intensity of the reaction peaks is more clearly shown by curve D-2-b. The increase in peak intensity of the endothermic reactions cannot be explained, as was done in the case of kaolinite, by the change in the amount of the material tested. Actual weight measurements were made to confirm the fact that the amount of bentonite tested decreased with decreasing grain size.

ILLITE: It can be seen from appended curves D-3-a and D-3-b that the variation of grain size has the same effect on the illite differential thermal curves as on those of bentonite. This would be expected since both minerals have similar lattice structures (2:1 lattice).

We want to emphasize the fact that the grain size effects with kaolinite are the reverse of those with bentonite and illite.

It might be interesting to note that kaolinite shrinks during testing a relatively small amount as compared to bentonite and illite. Also the color of kaolinite is not visibly altered by the test, whereas bentonite changes from a very light brown to a light orange-brown and illite changes from gray to dark orange-brown.

THE STANDARD DIFFERENTIAL THERMAL CURVES (See Appendix E)

Standard differential thermal curves have been made for each grain size of the three clay minerals using a heating rate of 1023°C/Hr. The number, type, temperature, and intensity of the deflections on these curves are characteristic of each clay mineral, therefore, the curves can be readily utilized in qualitative analyses. Furthermore, in the following paragraphs, we will develop a method whereby these curves can be used to analyze quantitatively mixtures of the clay minerals.

QUANTITATIVE ANALYSIS UTILIZING DIFFERENTIAL THERMAL CURVES

Deflections of the differential thermal curve represent energy changes, i.e., the heat energy adsorbed or liberated. As pointed out by Norton (6), the area under a peak is a direct measure of the quantity of heat involved. Therefore, a mixture of clay minerals can be analyzed quantitatively by comparing the areas under the reaction peaks of its differential thermal curve with the areas under the corresponding peaks of standard differential thermal curves of its constituent clays. This method, satisfactory for mixtures whose curves contain only isolated peaks, becomes very complex and time consuming

when analyzing mixtures from curves on which the reaction peaks are merged or overlapped. A method utilizing peak ordinates would greatly facilitate computations. To study the effect of the amount of material on peak ordinates, we ran a series of tests using reduced percentages of clay mineral, accomplished by mixing the clays with inert material (calcined alumina). Refer to curves F-1-a, b, and c. A plot of the intensity of peak ordinates against percentage of clay mineral (curve F-1-d) shows the relationship to be very close to linear. The assumption that peak ordinates are directly proportional to the percentage of clay mineral, experimentally justified, will be used in all following analyses.

Since the deflection peaks are approximately triangular, our analyses are based on properties of triangular areas, either isolated or superimposed. In Figures I and II on page 23, (a), (b), and (c) represent, respectively, differential thermal curves of A, B, and a mixture of A and B. Figure I will be used to develop the method of analyzing mixtures whose curves contain isolated peaks. The general equations - wherein x and y represent, respectively, the percentages of A and B

in the mixture - for this condition are:

$$Hx = H''$$

$$h'y = h''$$

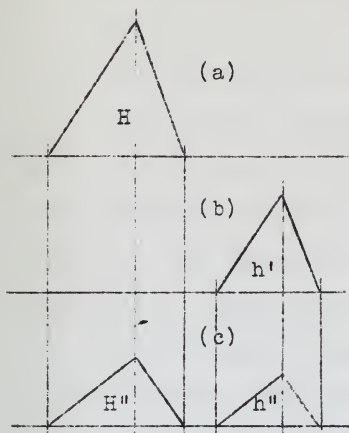


FIGURE I

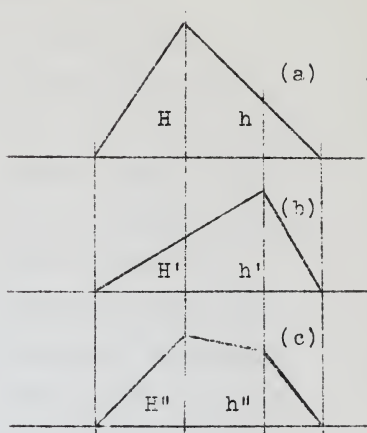


FIGURE II

FIGURE II will be used to develop the method of analyzing mixtures whose curves contain superimposed peaks. The general equations for this condition are:

$$Hx + H'y = H''$$

$$hx + h'y = h''$$

In addition, analyses will be made using curve areas bounded vertically 20°C on either side of the peak ordinates. Actually, these areas are only modified ordinates and can be used in the above equations.

Thus, we have four methods of solution - all are similar, yet each differs in the use of:

1. Ordinates of isolated peaks
2. Ordinates of superimposed peaks
3. Modified ordinates of isolated peaks
4. Modified ordinates of superimposed peaks

To facilitate computations, the ordinates and modified ordinates of the reaction peaks of the standard mixture curves have been tabulated (Tables A and B). The baseline for the ordinates of kaolinite is taken as the horizontal portion of the curve between the endothermic and exothermic reaction peaks. Similarly, the baseline for the bentonite and illite ordinates is taken as the horizontal tangent to the curve between the second and third endothermic reaction peaks.

For brevity, only detailed analysis of Mixture #4 will be presented.

SAMPLE COMPUTATION

Mixture #4: 50% Kaolinite - 50% Bentonite (100-140)

A qualitative analysis (visual inspection of differential thermal curve) of this mixture indicates the presence of kaolinite and bentonite. Therefore, the standard curves of these two clay minerals will be used in conjunction with the mixture curve in all methods of analysis.

TABLE A
TEMPERATURES AND ORDINATES OF REACTION PEAKS ON STANDARD
DIFFERENTIAL THERMAL CURVES FOR CLAY MINERALS
GRAIN SIZE RANGE (100-140) SEE APPENDIX E

TYPE OF REACTION	REACTION PEAK TEMPERATURE (°C)	CLAY MINERAL	ORDINATE (m.v.)	MODIFIED ORDINATE (m.v.-°C)	CORRESPONDING ORDINATES OF OTHER CLAY MINERALS*	
					Kaolinite Ord. Mod.Ord.	Bentonite Ord. Mod.Ord.
ENDOTHERMIC	610	KaOLINITE	-0.82	-30.50	--	0.01 -0.10
ENDOTHERMIC	720	BENTONITE	-0.32	-11.90	-0.03	--
ENDOTHERMIC	920	BENTONITE	-0.08	- 2.65	0.00	--

NOTE: All ordinates are measured in millivolt equivalents of the chromel-alumel thermocouples. The modified ordinates, measured in millivolt-degrees centigrade, are actually areas under the differential thermal curve bounded vertically 20°C, on either side of the peak ordinates.

*A corresponding ordinate of clay mineral 3 is that ordinate on its standard differential thermal curve at the temperature corresponding to that of a reaction peak on the standard differential thermal curve of A.

TABLE B
TEMPERATURES AND ORDINATES OF REACTION PEAKS ON THE DIFFERENTIAL
THERMAL CURVES OF MIXTURES OF CLAY MINERALS - GRAIN SIZE
RANGE (100-140) SEE APPENDIX F

MIXTURE	ORD. at KAOL. ENDO. PEAK	M.O. at KAOL. ENDO. PEAK	ORD. at BENT. 2nd ENDO. PEAK	M.O. at BENT. 2nd ENDO. PEAK	ORD. at BENT. 3rd ENDO. PEAK	M.O. at BENT. 3rd ENDO. PEAK
1	-0.36	-12.95	---	---	---	---
2	---	---	-0.16	-5.70	-0.04	-1.20
3	-0.69	-25.20	-0.16	-5.90	-0.01	-0.32
4	-0.42	-15.40	-0.21	-7.30	-0.04	-1.10
5	-0.21	-7.35	-0.27	-9.35	-0.06	-2.00
6	-0.21	-7.40	-0.19	-6.50	-0.03	-0.90

MIXTURE #1: 50% KAOLINITE, 50% ALUMINA
MIXTURE #2: 50% BENTONITE, 50% ALUMINA
MIXTURE #3: 75% KAOLINITE, 25% BENTONITE
MIXTURE #4: 50% KAOLINITE, 50% BENTONITE
MIXTURE #5: 25% KAOLINITE, 75% BENTONITE
MIXTURE #6: 25% KAOLINITE, 50% BENTONITE, 25% ALUMINA

NOTE: All ordinates are measured in millivolt-equivalents of the chromel-alumel thermocouples; the modified ordinates are measured in millivolt-degrees centigrade.

Method 1: (Using 3rd Endothermic peak of bentonite).

$$h'y = h'' \quad (y = \% \text{ Bentonite})$$

$$0.08 y = 0.04$$

$$y = 50.0\% \text{ Bentonite}$$

In the above equation h' is the ordinate of the third endothermic peak on the standard differential thermal curve of bentonite (100-140) as listed in Table A and h'' is the corresponding ordinate on the curve of mixture #4, listed in Table B.

METHOD 3: (Using 3rd endothermic peak of Bentonite)

$$h'y = h'' \quad (y = \% \text{ Bentonite})$$

$$2.65 y = 1.10$$

$$y = 41.6\% \text{ Bentonite}$$

The values of the modified ordinates h' and h'' are listed in Tables A and B, respectively.

METHOD 2: (Using 1st endothermic peak of kaolinite and 2nd endothermic peak of Bentonite).

$$Hx + H'y = H'' \quad (x = \% \text{ kaol.}, y = \% \text{ bent.}).$$

$$hx + h'y = h''$$

$$0.82x + 0.01y = 0.42$$

$$0.03x + 0.32y = 0.21$$

$$x = 51.3\% \sim 52.2\% \text{ Kaol.}$$

$$h = \frac{47.0}{98.3\%} \sim \frac{47.8}{100.0\%} \text{ Bent.}$$

The values of the ordinates H and h (kaolinite) and H' and h' (bentonite) are listed in Table A. The values of the ordinates H'' and h'' are listed in Table B. Since the total percentage of the mixture

as computed by the general equation is less than 100%, we feel justified in adjusting the percentages of both clay minerals.

METHOD 4: (Using 1st endothermic peak of kaolinite and the 2nd endothermic peak of bentonite).

$$Hx + H'y = H'' \quad (x = \% \text{ kaol.}, y = \% \text{ bent.})$$

$$hy + h'y = h''$$

$$\underline{30.50x + 0.10y = 15.40}$$

$$\underline{1.10x + 11.90y = 7.30}$$

$$x = 50.5\% \sim 47.2\% \text{ Kaol.}$$

$$y = \frac{56.6}{107.1\%} \sim \frac{52.8}{100.0\%} \text{ Bent.}$$

The values of the modified ordinates H and h (kaolinite) and H' and h' (bentonite) are listed in Table A; H'' and h'' are listed in Table B.

The results of quantitative analyses of all mixtures are compiled in Table C. It should be noted that the largest errors occur when Methods 1 and 3 are used in analyzing mixtures from the third endothermic peak of bentonite. This is very likely due to the fact that an error in determining the ordinate or modified ordinate of this relatively small peak will greatly magnify the error in the calculated percentage of the clay mineral in the mixture.

By comparing the results of the methods based.

on ordinates and modified ordinates, we can see no justification for using the more laborious methods involving modified ordinates.

As has been shown, a quantitative analysis from differential thermal curves is simple, fast and economical. If a laboratory possesses standard curves of all clay minerals, an analysis of a mixture of these clays could be made in a matter of minutes, simply by utilizing ordinates from the machine plotted curve of the mixture in the solution of the general equations.

GENERAL NOTE

We would like to point out that our differential thermal curves of illite indicate a small exothermic reaction at approximately 420°C. We found no mention of this reaction by other investigators.

TABLE C

QUANTITATIVE ANALYSES UTILIZING DIFFERENTIAL
THERMAL CURVES

MIXTURE No.	PREPARED* PROPORTIONS	METHOD OF SOLUTION#	CALCULATED PROPORTIONS	ERROR (%)
1	50%K-50%A	1	44.0%K	6.0
		3	42.5%K	7.5
2	50%B-50%A	1	50.0%B	0.0
		3	46.6%B	3.4
3	75%K-25%B	1	12.5%B	12.5
		3	12.1%B	12.9
		2	67.5K-32.5B	7.5
		4	66.4K-33.6B	8.6
4	50%K-50%B	1	50.0%B	0.0
		3	41.6%B	8.4
		2	52.2K-47.8B	2.2
		4	47.2K-52.8B	2-8
5	25%K-75%B	1	75.0%B	0.0
		3	75.5%B	0.5
		2	24.1K-75.9B	0.9
		4	24.0K-76.0B	1.0
6	25%K-50%B- 25%A	1	37.5%B	12.5
		3	34.0%B	16.0
		2	25.7K-56.0B	0.7&6.0
		4	24.3K-52.3B	0.7&2.3

*K = Kaolinite, B = Bentonite, A = Alumina

For description of methods, see page 24

TABLE 1

Summary of the results of the analysis of variance for the effect of the treatment on the response of the subjects to the test.

Source of variation		df	Mean square	F	Prob
Between groups		1	1.00	1.00	0.32
Within groups		19	0.10	0.10	0.75
Total		20	1.10		
Error		19	0.10		
Grand total		20	1.10		

NOTE: The results of the analysis of variance for the effect of the treatment on the response of the subjects to the test are shown in Table 1. The results of the analysis of variance for the effect of the treatment on the response of the subjects to the test are shown in Table 1.

RECOMMENDATIONS

We highly recommend that more sensitive equipment be installed to better control the heating rate. The present mechanical control equipment permits too great a differential between the temperature of the thermal standard and the temperature required to maintain the desired rate of heating. Possibly more sensitive mechanical control equipment would be satisfactory; however, we believe an electronic control unit should be installed.

From curves D-1-b, D-2-b, and D-3-b, it can be seen that there is a tendency for the reaction peaks to reach a limiting intensity with decreasing grain size. We suggest that tests be made on finer fractions (below 200 mesh sieve) to determine the limiting values of the peak ordinates of these clay minerals.

From our investigations, we feel justified in assuming a linear relation between peak intensity and amount of material tested. However, we suggest that further investigation be made to more conclusively establish this relationship.

Some investigators believe that the loss of lattice water from clay minerals is a reversible process, i.e., the lattice water lost by heating can be reinstated to its original position in the

clay structure, if the proper conditions exist. A study of this, which should prove interesting, could easily be made with our equipment. If a clay mineral, which has been heated beyond the point at which lattice water is driven off but not to the point at which the lattice structure is destroyed, is placed in a warm saturated atmosphere for varying periods of time, subsequent retesting should indicate the validity of their assumption.

REFERENCES

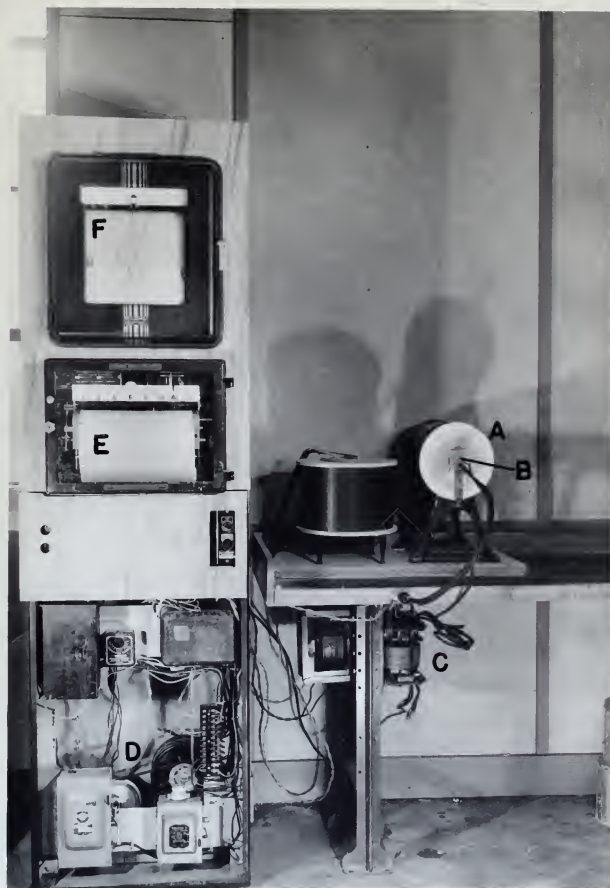
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APPENDICES

- A. Photographs of Equipment
- B. Record of Tests Conducted
- C. Effect of variation in Heating Rate on the
Differential Thermal Curve of Kaolinite
- D. Effect of Variation in Grain Size on the
Differential Thermal Curves
- E. Standard Differential Thermal Curves
- F. Differential Thermal Curves of Prepared Mixtures

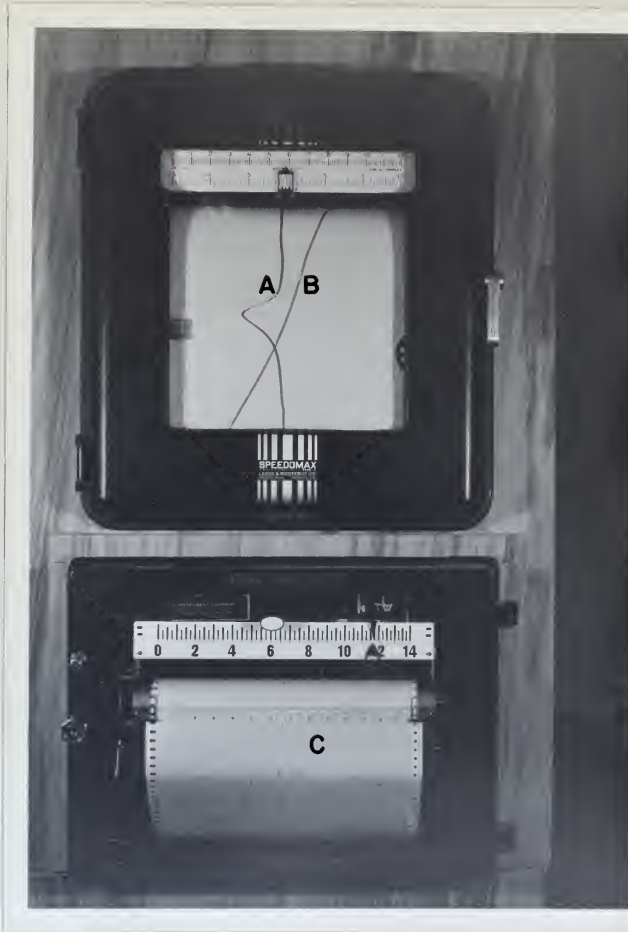
APPENDIX A
PHOTOGRAPHS OF EQUIPMENT

DIFFERENTIAL THERMAL ANALYSIS
TEST EQUIPMENT



- A. Furnace
- B. Specimen Holder
- C. Furnace Transformer
- D. Variac
- E. Brown Potentiometer
- F. Leeds and Northrup Speedomax

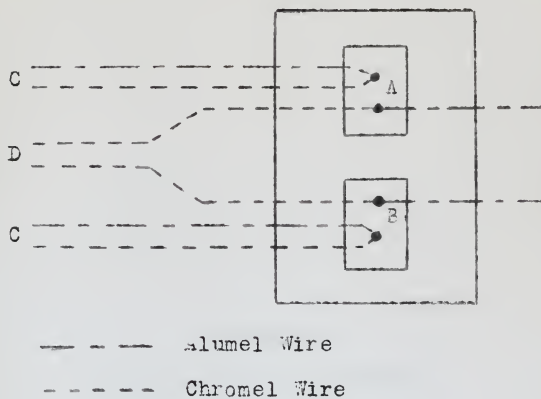
DIFFERENTIAL THERMAL ANALYSIS
RECORDING EQUIPMENT



THERMAL CURVES

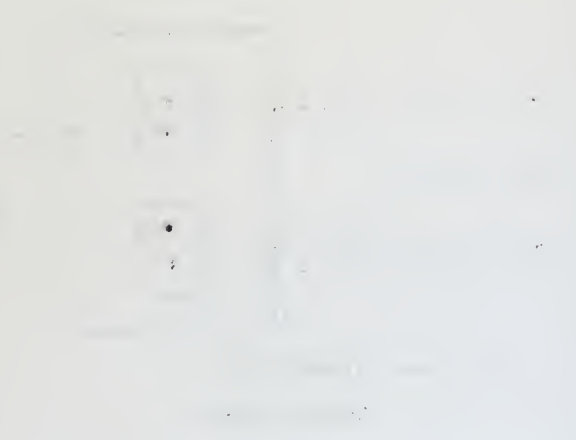
- A. Differential Thermal Curve
- B. Thermal Curve of Test Mineral
- C. Thermal Curve of Thermal Standard

DIFFERENTIAL THERMAL ANALYSIS
SCHEMATIC DIAGRAM OF SPECIMEN HOLDER



- A. Test Sample Well
- B. Thermal Standard Well
- C. Temperature Thermocouples
- D. Differential Temperature Thermocouple

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APPENDIX B
RECORD OF TESTS CONDUCTED

DIFFERENTIAL THERMAL ANALYSIS TEST RECORD

TEST SPECIMEN TYPE	GRAIN SIZE	ALUMINA GRAIN SIZE	HEAT RATE °C/hr.	NUMBER OF TESTS
KAOLINITE	140-200	140-200	598	2
	140-200	140-200	837	2
	140-200	140-200	898	2
	140-200	140-200	951	2
	140-200	140-200	1023	4
	140-200	140-200	1099	2
	140-200	140-200	1160	3
	140-200	140-200	1352	2
ALUMINA	60-100	60-100	1023	7
	100-140	60-100	1023	-
	140-200	60-100	1023	-
	200-Fan	60-100	1023	2
KAOLINITE	60-100	60 Mesh	1023	-
	60-100	60-100	1023	3
	100-140	60 Mesh	1023	2
	100-140	100-140	1023	6
	140-200	60 Mesh	1023	2
	140-200	140-200	1023	4
	200-Fan	60 Mesh	1023	1
	200-Fan	200-Fan	1023	4
BENTONITE	60-100	60-100	1023	3
	100-140	100-140	1023	3
	140-200	140-200	1023	3
	200-Fan	200-Fan	1023	3
ILLITE	60-100	60-100	1023	3
	100-140	100-140	1023	3
	140-200	140-200	1023	3
	200-Fan	200-Fan	1023	3

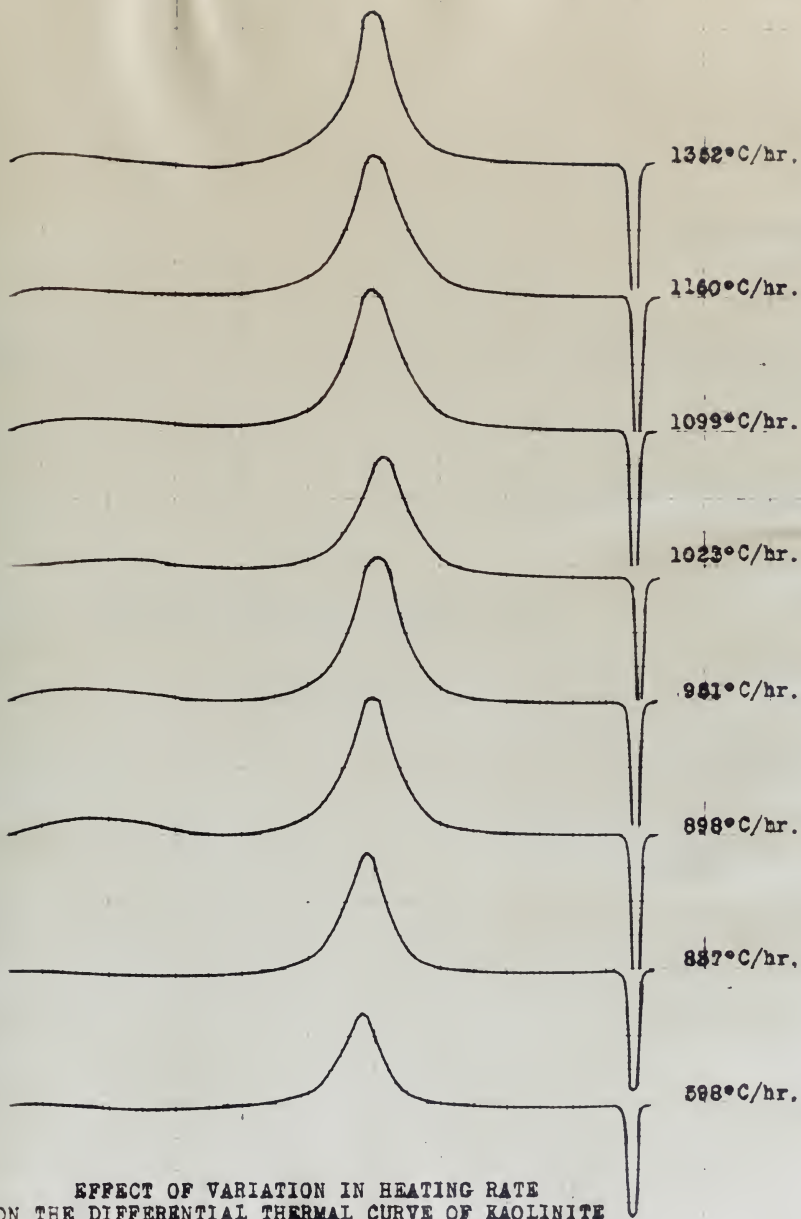
DIFFERENTIAL THERMAL ANALYSIS TEST RECORD

TEST SPECIMEN		ALUMINA	HEAT RATE	NUMBER
TYPE	GRAIN SIZE	GRAIN SIZE	°C/hr.	OF TESTS
MIXTURE #1	100-140	100-140	1023	2
MIXTURE #2	100-140	100-140	1023	2
MIXTURE #3	100-140	100-140	1023	3
MIXTURE #4	100-140	100-140	1023	3
MIXTURE #5	100-140	100-140	1023	3
MIXTURE #6	100-140	100-140	1023	3

MIXTURE #1: 50% KAOLINITE, 50% ALUMINA
 MIXTURE #2: 50% BENTONITE, 50% ALUMINA
 MIXTURE #3: 75% KAOLINITE, 25% BENTONITE
 MIXTURE #4: 50% KAOLINITE, 50% BENTONITE
 MIXTURE #5: 25% KAOLINITE, 75% BENTONITE
 MIXTURE #6: 25% KAOLINITE, 50% BENTONITE,
 25% ALUMINA

APPENDIX C

EFFECT OF VARIATION IN THE HEATING RATE
On the
DIFFERENTIAL THERMAL CURVE OF KAOLINITE



Millivolt Equivalents - 1" = 0.8 m.v.

EFFECT OF VARIATION IN HEATING RATE
ON THE DIFFERENTIAL THERMAL CURVE OF KAOLINITE

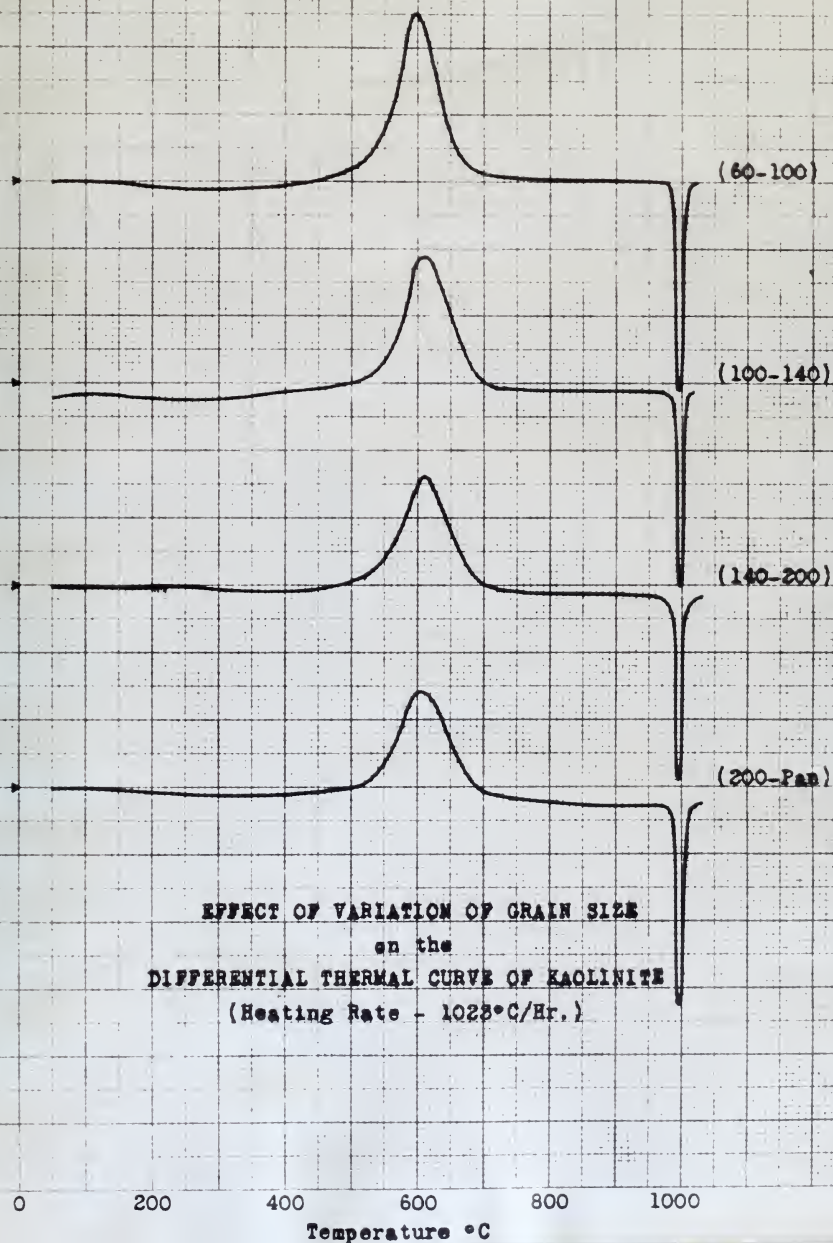
0 200 400 600 800 1000
Temperature-°C.

APPENDIX D

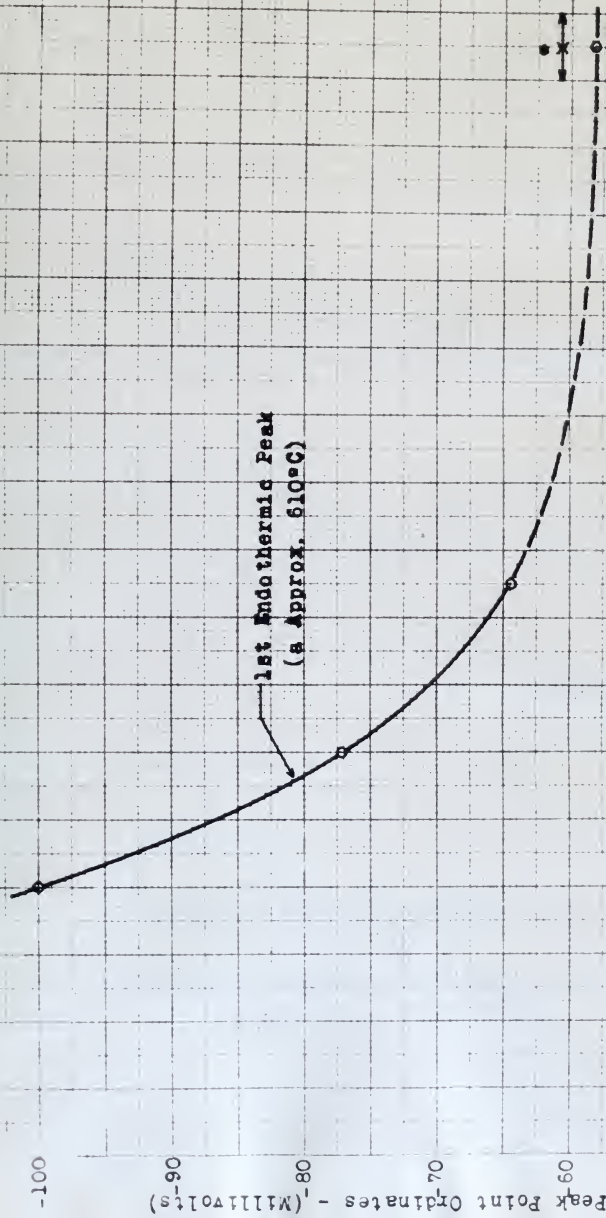
EFFECT OF VARIATION IN GRAIN SIZE ON THE DIFFERENTIAL THERMAL CURVE

1. Kaolinite
2. Bentonite
3. Illite

Millivolt Equivalents - 1" = 0.80 mv



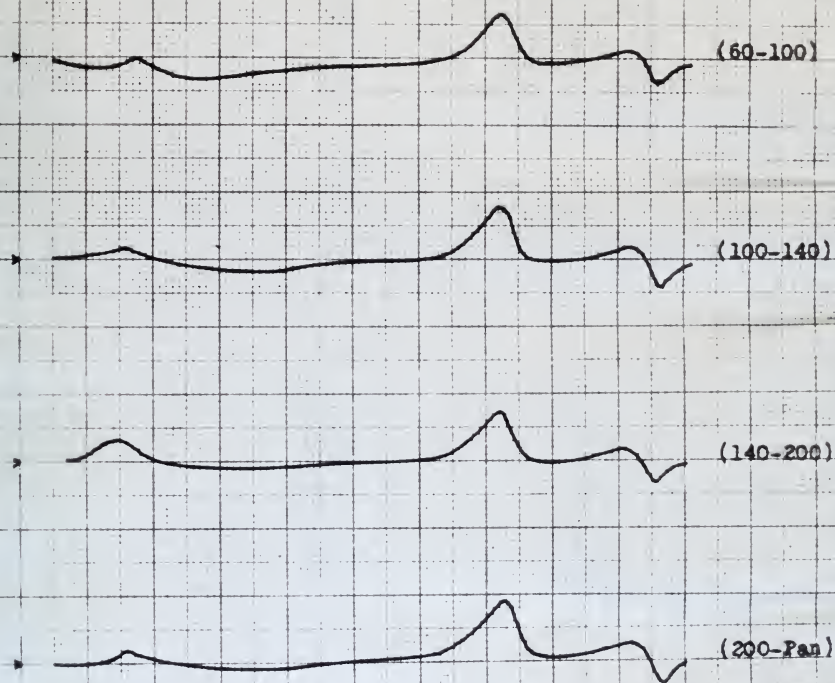
EFFECT OF VARIATION OF GRAIN SIZE
on the
DIFFERENTIAL THERMAL CURVE OF KAOLINITE
(Heating Rate - 1025°C/Hr.)



EFFECT OF GRAIN SIZE ON PEAK ORDINATE OF KAOLINITE

Average Grain Size Plotted for Each Fraction
 Average Grain Size for 200-Pass Fraction Not Known
 And The Abscissa of This Point is Arbitrarily Plotted

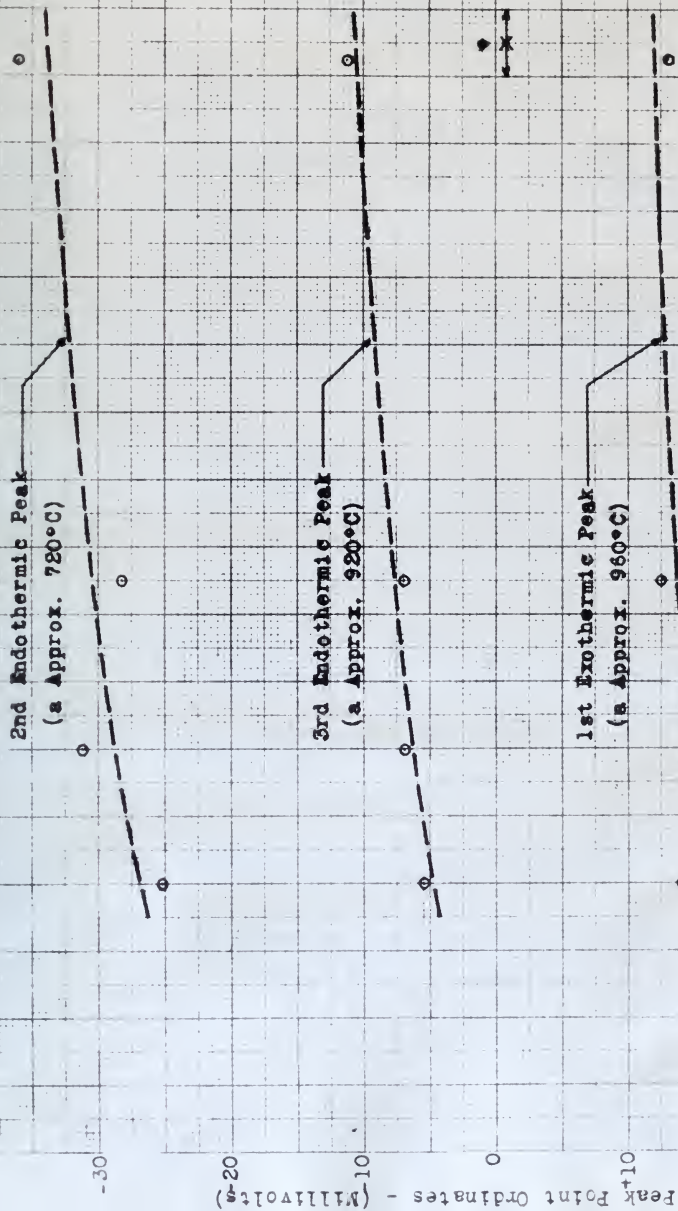
Grain Size - (By U. S. Standard Sieve #)



Millivolt Equivalents - 1" = 0.80 mv

EFFECT OF VARIATION OF GRAIN SIZE
on the
DIFFERENTIAL THERMAL CURVE OF BENTONITE
(Heating Rate - 1023°C/Hr.)

0 200 400 600 800 1000
Temperature °C



EFFECT OF GRAIN SIZE ON PEAK ORDINATES OF BENTONITE

Average Grain Size Plotted for Each Fraction
 *Average Grain Size for 200-mesh Fraction Not Known
 And The Abscissa of This Point is Arbitrarily Plotted

Grain Size - (By U. S. Standard Sieve #)

(60-100)

(100-140)

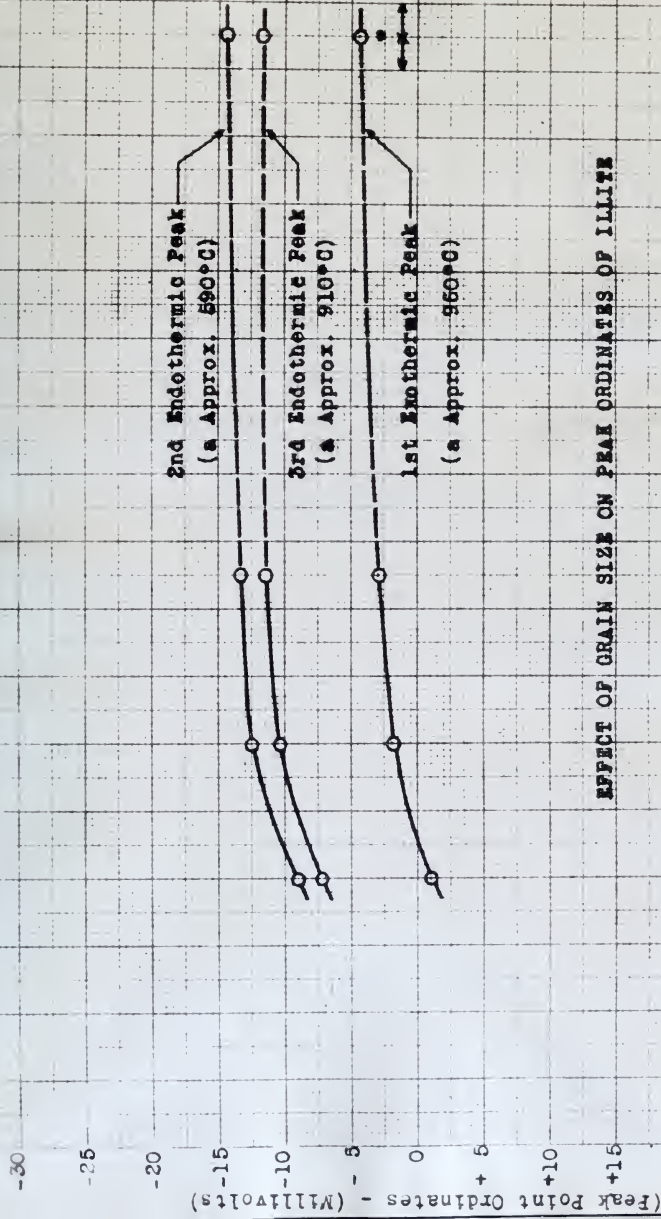
(140-200)

(200-Pan)

Millivolt Equivalents - 1" = 0.80 mV

EFFECT OF VARIATION OF GRAIN SIZE
on the
DIFFERENTIAL THERMAL CURVE OF ILLITE
(Heating Rate - 1023°C/Hr.)

0 200 400 600 800 1000
Temperature-°C



EFFECT OF GRAIN SIZE ON PEAK ORDINATES OF ILLITE

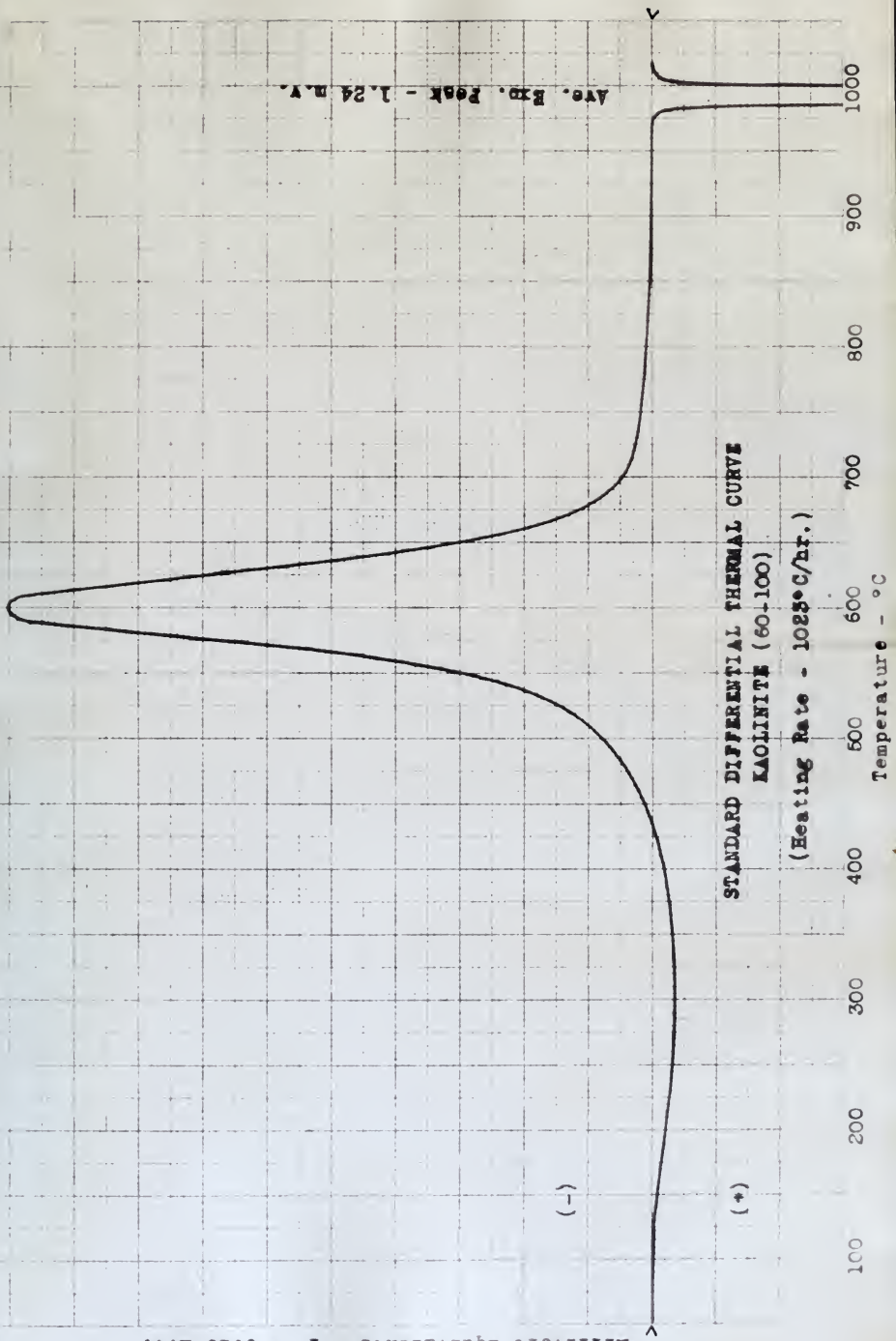
Average Grain Size Plotted for Each Fraction
 *Average Grain Size for 200-Pan Fraction Not Known
 And The Abscissa of This Point is Arbitrarily Plotted

APPENDIX E

STANDARD DIFFERENTIAL THERMAL CURVES

1. Kaolinite
2. Bentonite
3. Illite

Millivolt Equivalents - 1" = 0.20 m.v.



Millivolt Equivalents - 1" = 0.20 m.v.

(-)

(+)

STANDARD DIFFERENTIAL THERMAL CURVE

KAOLINITE (100-140)

(Heating Rate - 1023°C/hr.)

Temperature - °C

100

200

300

400

500

600

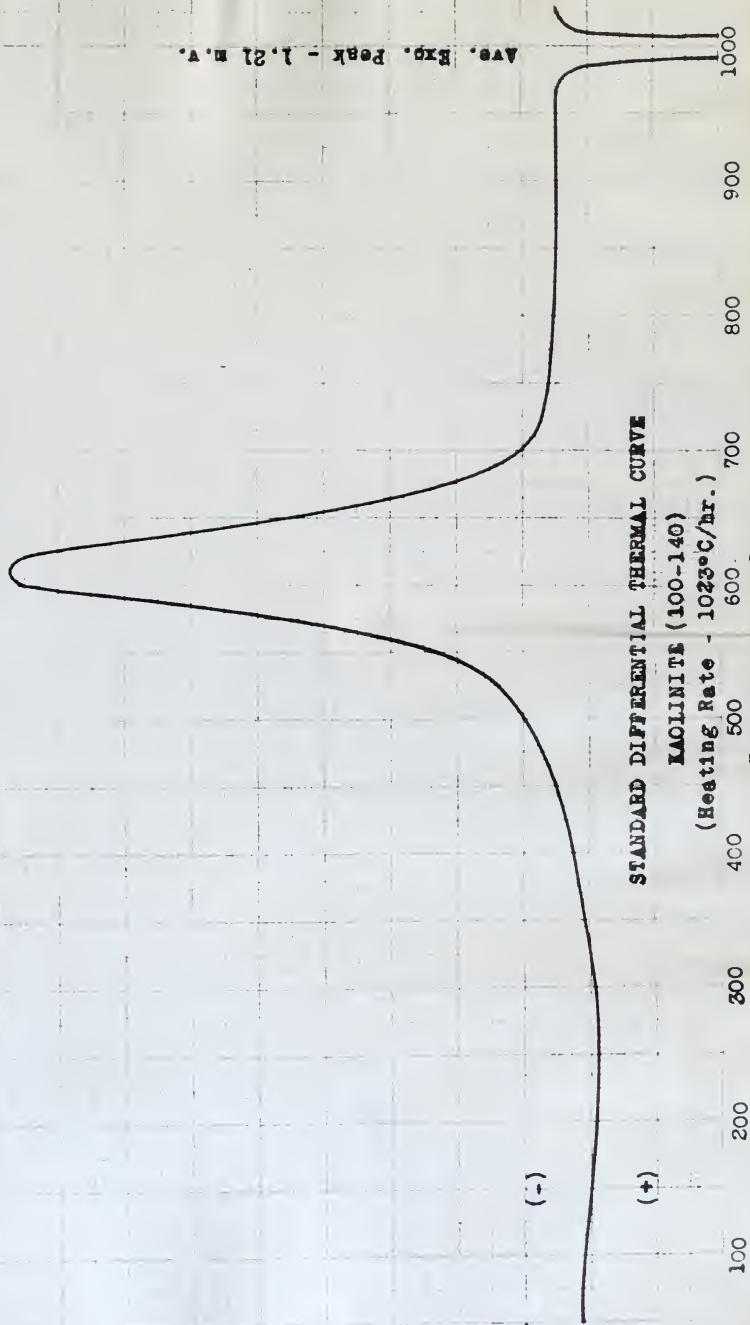
700

800

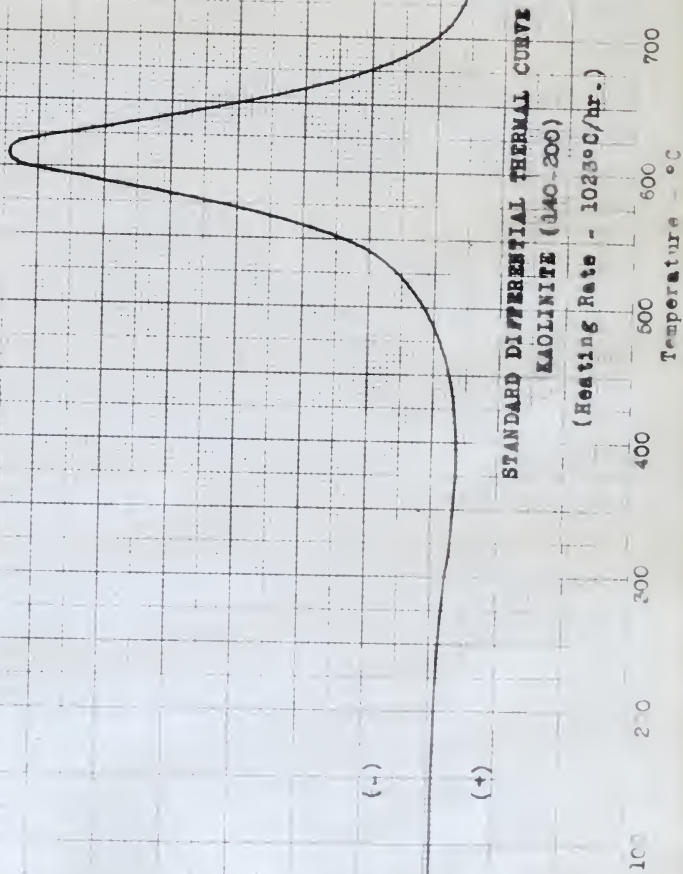
900

1000

Ave. Exo. Peak - 1.21 m.v.

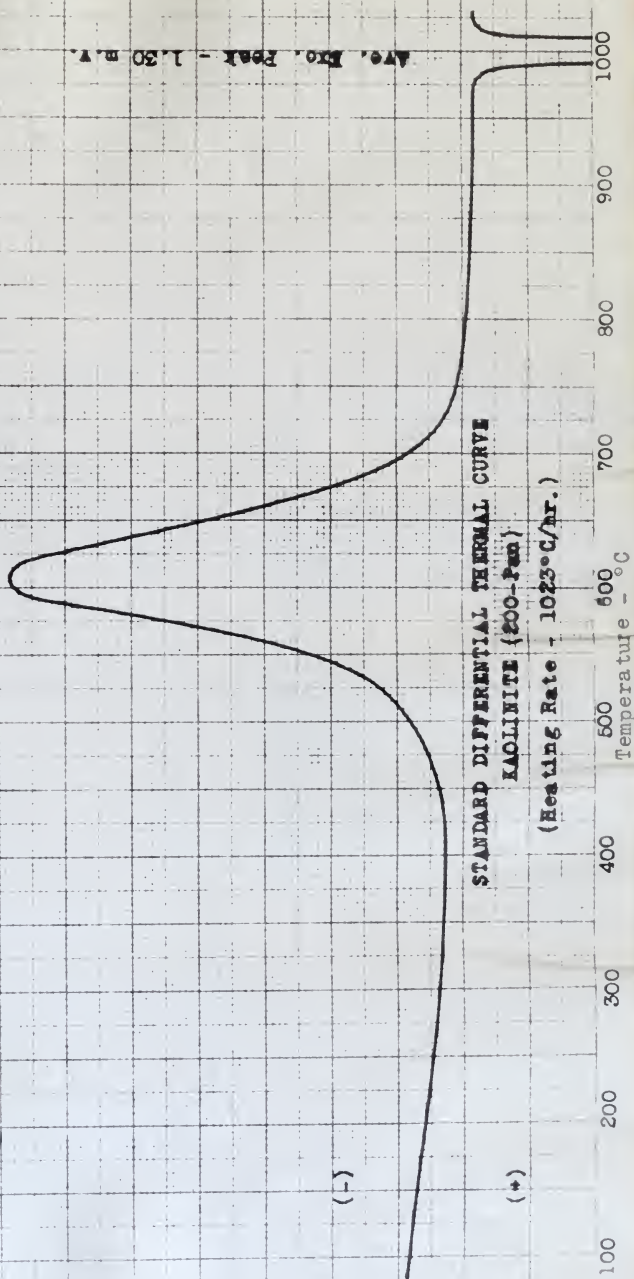


Millivolt Equivalents - 1" = 0.20 m.v.



Avg. Exo. Peak - 1.16 m.v.

Millivolt Equivalents - 1" = 0.20 m.v.



Millivolt Equivalents - 1" = 0.20 m.v.

STANDARD DIFFERENTIAL THERMAL CURVE
BENTONITE (60-100)
(Heating Rate - 1023°C/hr.)

(-)

(+)

100 200 300 400 500 600 700 800 900 1000
Temperature - °C

M1111 Volt Equivalents - 1" = 0.20 m.v.

(-)

(+)

STANDARD DIFFERENTIAL THERMAL CURVE
BENTONITE (100.140)
(Heating Rate - 1023°C/hr.)

Temperature - °C

100

200

300

400

500

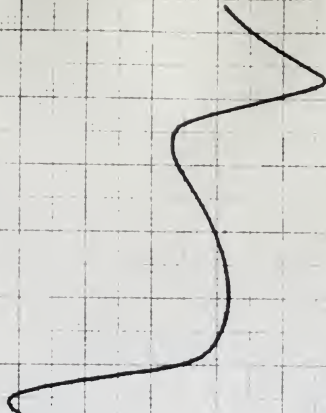
600

700

800

900

1000



Millivolt Equivalents - 1" = 0.20 m.v.

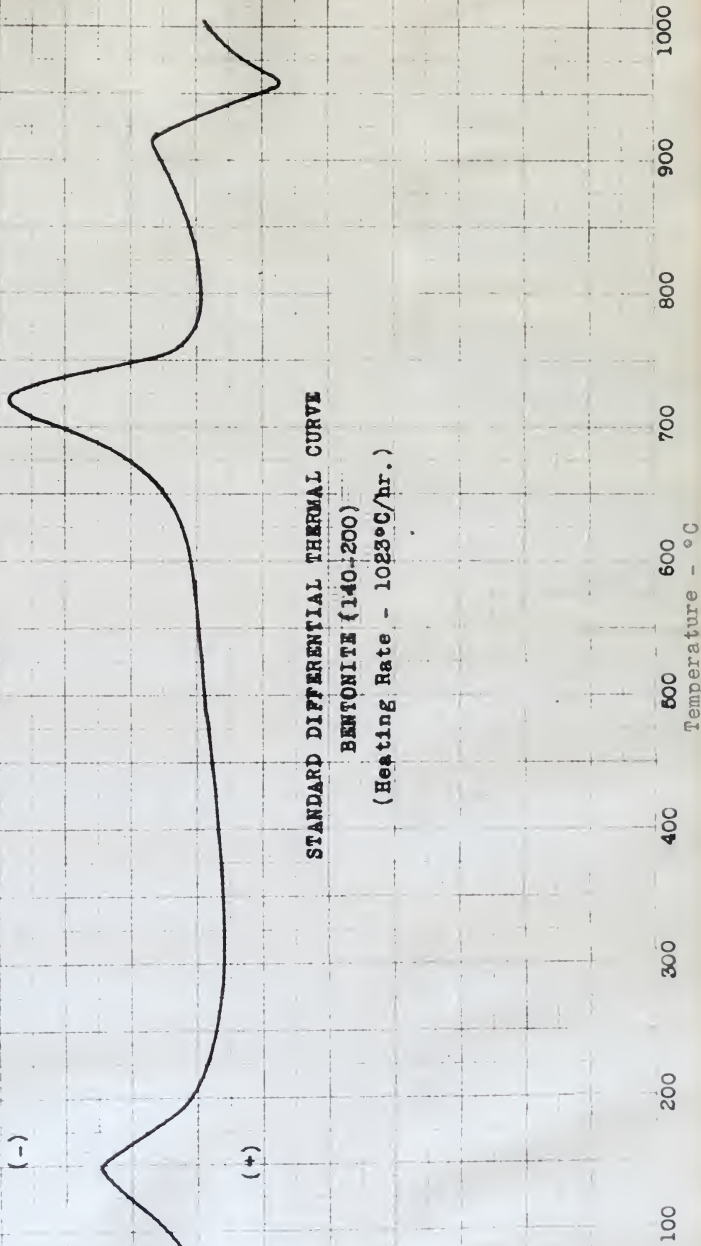
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STANDARD DIFFERENTIAL THERMAL CURVE

BENTONITE (140-200)

(Heating Rate - 1023°C/hr.)



Millivolt Equivalents - 1" = 0.20 m.v.

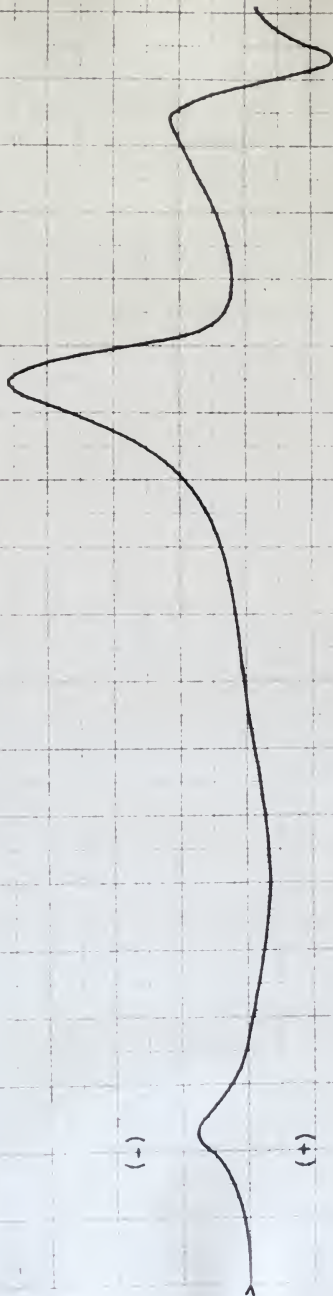
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STANDARD DIFFERENTIAL THERMAL CURVE

BENTONITE (200-Pan)

(Heating Rate - 1023°C/hr.)



100

200

300

400

500

600
Temperature - °C

700

800

900

1000

Millivolt Equivalents - 1" = 0.20 mV

(-)

(+)

STANDARD DIFFERENTIAL THERMAL CURVE

ILLITE (60-100)

(Heating Rate - 1023°C/Hr.)

Temperature-°C

0

100

200

300

400

500

600

700

800

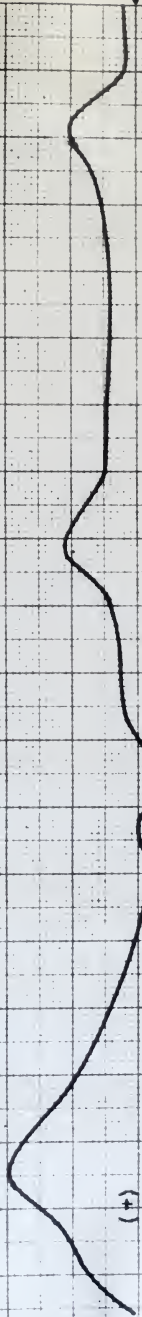
900

1000

Millivolt Equivalents - 1" = 0.20 mV

(-)

(+)



STANDARD DIFFERENTIAL THERMAL CURVE

ILLITE (100-140)

(Heating Rate = 1023°C/Hr.)

Temperature-°C

1000

900

800

700

600

500

400

300

200

100

Millivolt Equivalents - 1" = 0.20 mv

100

(-)

(+)

STANDARD DIFFERENTIAL THERMAL CURVE

ILLITE (140-200)

(Heating Rate - 1023°C/Hr.)

0

100

200

300

400

500

600

700

800

900

1000

Temperature - °C

Y

X

Millivolt Equivalents - 1" = 0.20 mV

(-)

(+)

STANDARD DIFFERENTIAL THERMAL CURVE

ILLITE (200-Fan)

(Heating Rate - 1023°C/Hr.)

Temperature-°C

0

100

200

300

400

500

600

700

800

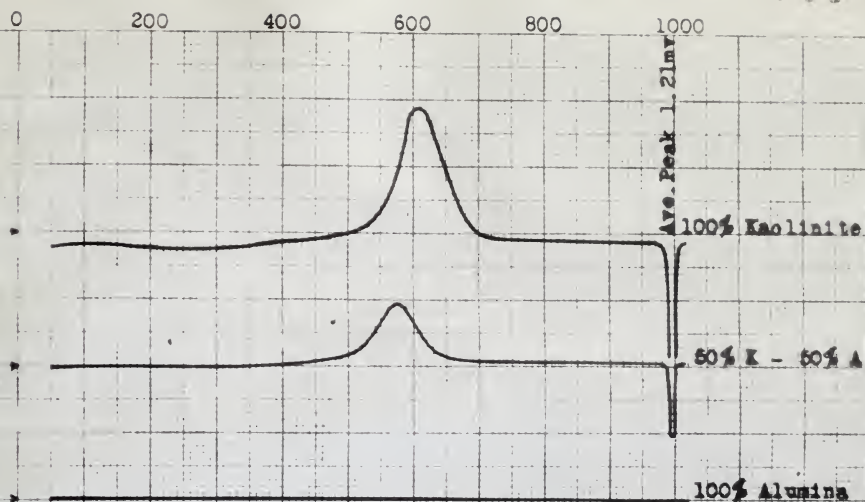
900

1000

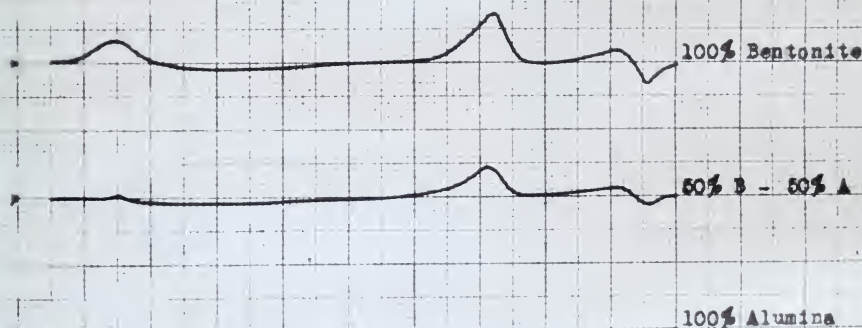
APPENDIX F

DIFFERENTIAL THERMAL CURVES OF PREPARED MIXTURES

1. (a) Kaolinite - Alumina
 (b) Bentonite - Alumina
2. Kaolinite - Bentonite
3. Kaolinite - Bentonite - Alumina



DIFFERENTIAL THERMAL CURVES
OF PREPARED MIXTURES OF KAOLINITE & ALUMINA
(100-140 Grain Size & Heating Rate 1023°C/hr.)



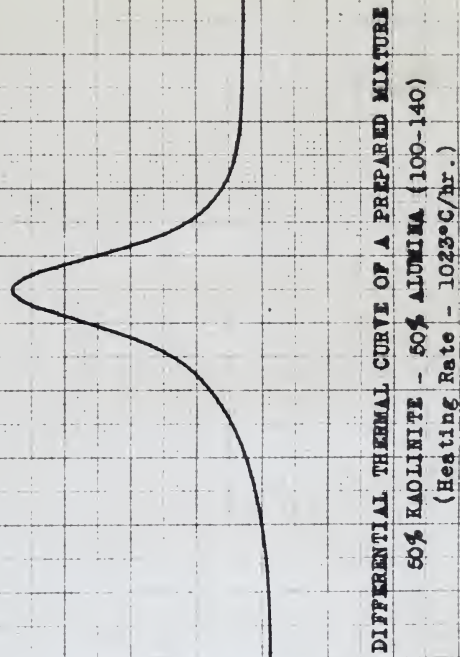
DIFFERENTIAL THERMAL CURVES
OF PREPARED MIXTURES OF BENTONITE AND ALUMINA
(100-140 Grain Size & Heating Rate 1023°C/Hr.)

0 200 400 600 800 1000

Temperature °C

Millivolt Equivalents - 1" = 0.80 mv

Millivolt Equivalents - 1" = 0.20 m.v.



Temperature - °C

100 200 300 400 500 600 700 800 900 1000

Ave. Exp. Peak, 41 m.v.

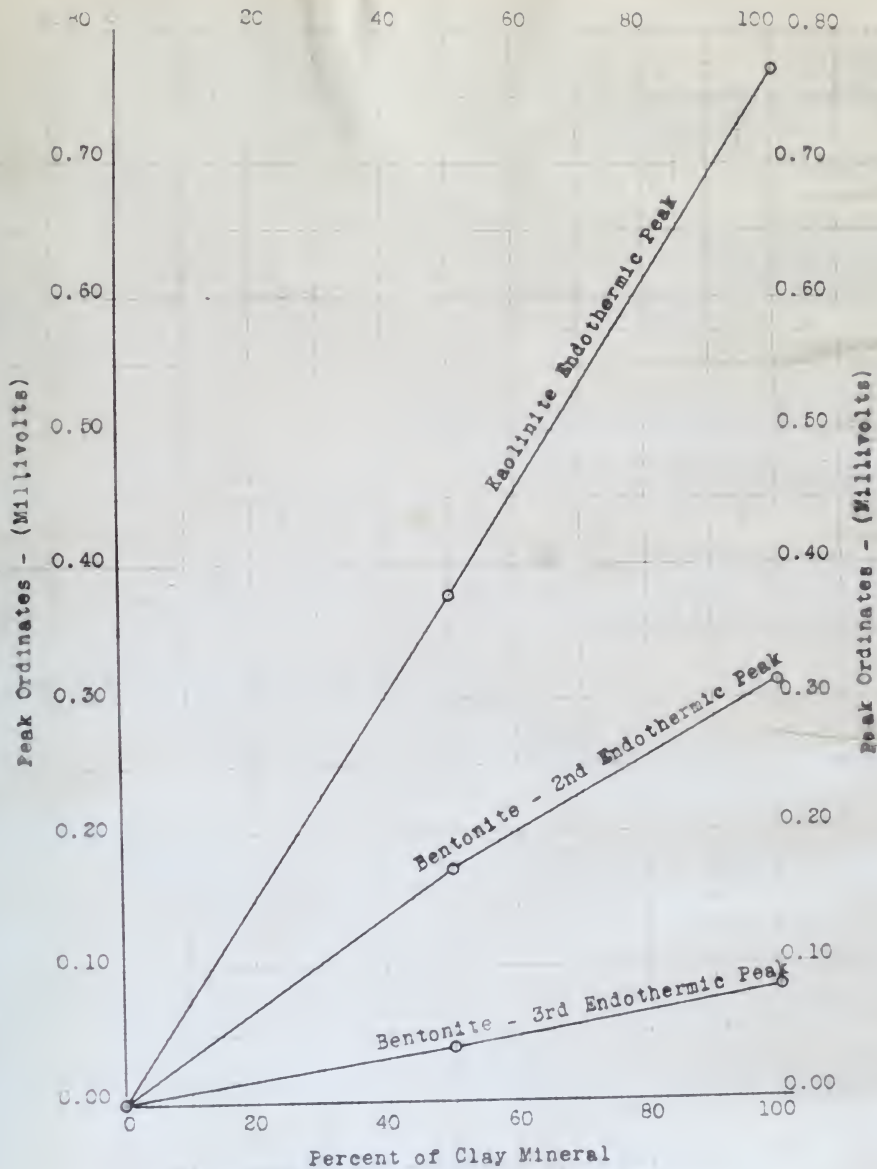
Millivolt Equivalents - $I'' = 0.20 \text{ m.v.}$

(-)

(+)

DIFFERENTIAL THERMAL CURVE OF A PREPARED MIXTURE
50% BENTONITE - 50% ALUMINA (100-140)
(Heating Rate - 1023°C/hr.)

100 200 300 400 500 600 700 800 900 1000
Temperature - $^{\circ}\text{C}$



EFFECT OF THE VARIATION IN THE AMOUNT OF CLAY MINERAL
ON THE PEAK ORDINATES

(100-140 Grain Size & 1023°C/Hr. Heating Rate)



Millivolt Equivalents - 1" = 0.80 mv

DIFFERENTIAL THERMAL CURVES
OF PREPARED MIXTURES OF KAOLINITE AND BENTONITE
(100-140 Grain Size & Heating Rate 1023°C/Hr.)

Millivolt Equivalents - 1" = 0.20 m.v.

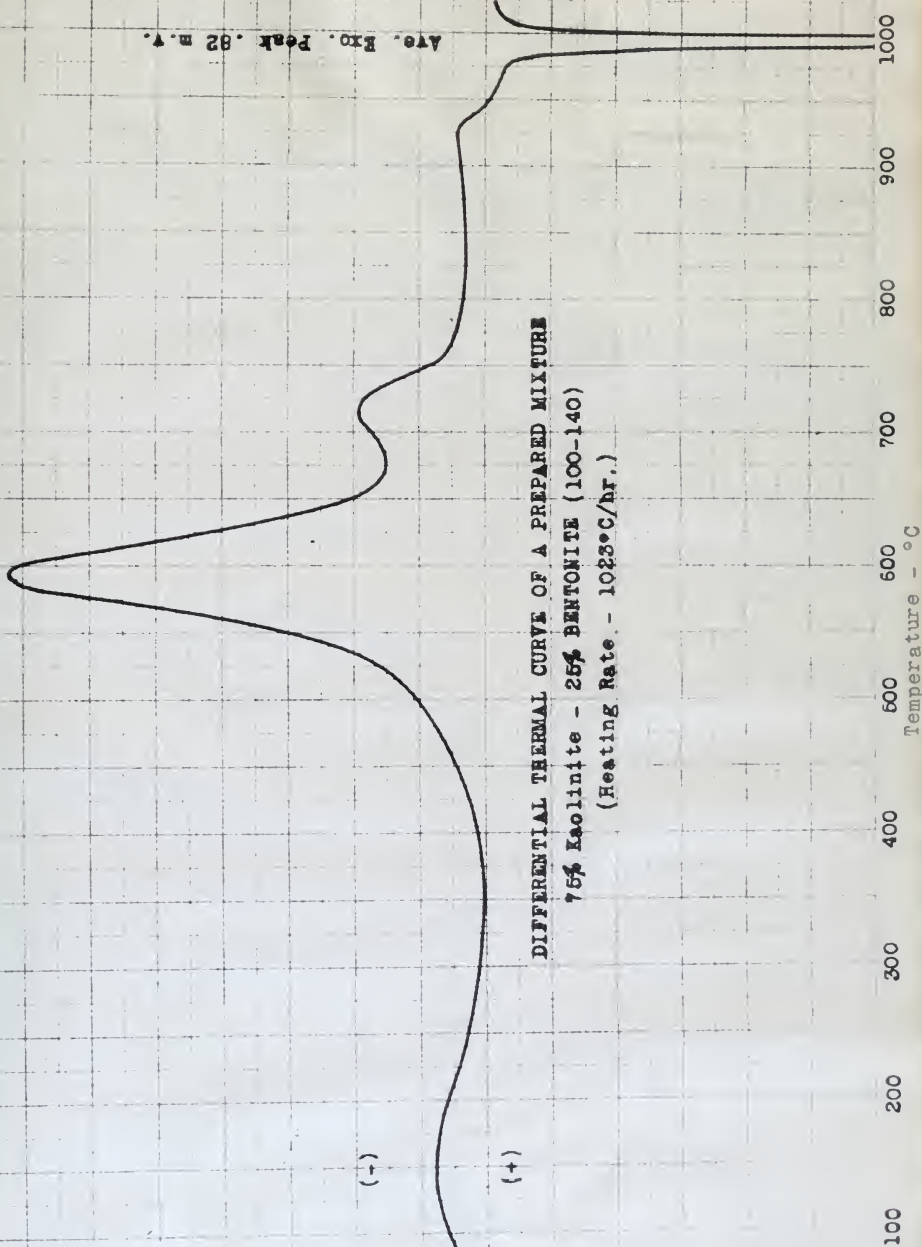
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DIFFERENTIAL THERMAL CURVE OF A PREPARED MIXTURE

75% Kaolinite - 25% BENTONITE (100-140)

(Heating Rate - 1023°C/hr.)



Ave. Exo. Peak .02 m.v.

Millivolt Equivalents - 1" = 0.20 m.v.

(-)

(+)

DIFFERENTIAL THERMAL CURVE OF A PREPARED MIXTURE
50% KAGLITE - 50% BENTONITE (100-140)
(Heating Rate - 1023°C/hr.)

Ave. Exo. Peak .42 m.v.

Temperature - °C

Millivolt Equivalents - 1" - 0.20 m.v.

(-)

(+)

DIFFERENTIAL THERMAL CURVE OF A PREPARED MIXTURE
25% KAOLINITE - 75% BENTONITE (100-140)
(Heating Rate - 1023°C/Hr.)

Temperature - °C

100

200

300

400

500

600

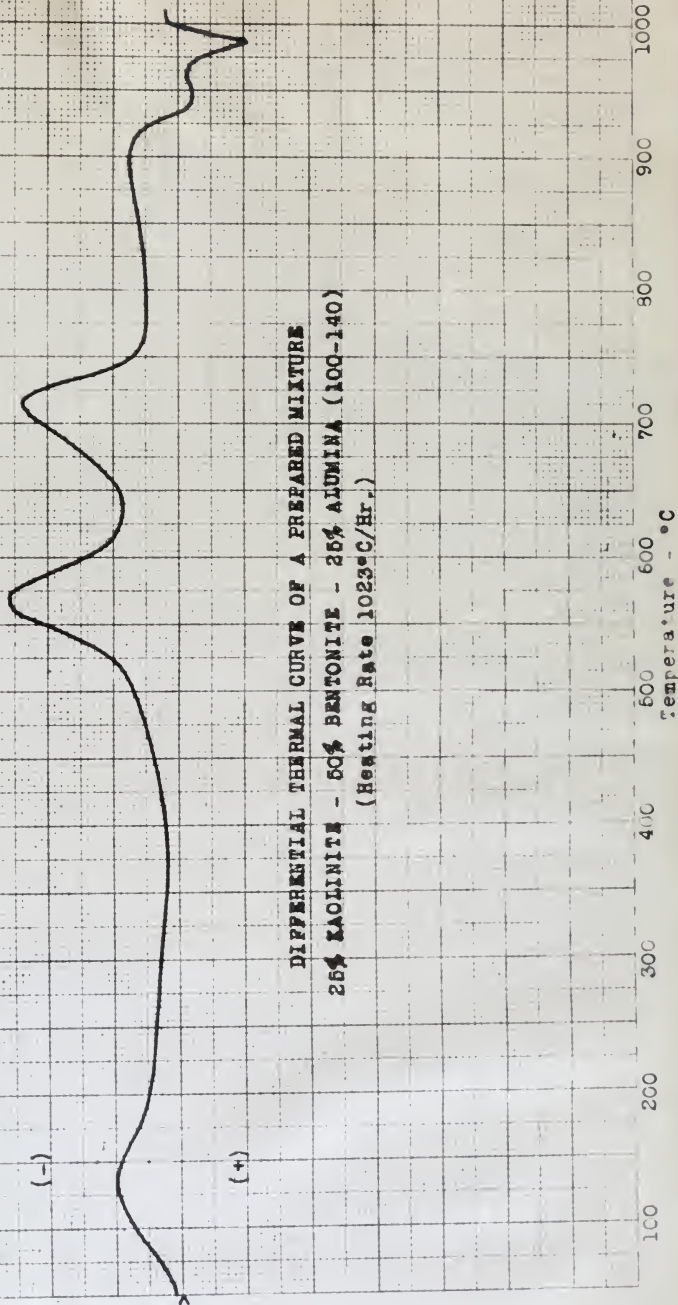
700

800

900

1000

Millivolt Equivalents - 1" = 0.20 mv



DIFFERENTIAL THERMAL CURVE OF A PREPARED MIXTURE

25% KAOLINITE - 50% BENTONITE - 25% ALUMINA (100-140)

(Heating Rate 1023°C/Hr.)

DATE DUE

This image shows a full page of blank graph paper. The grid consists of 20 columns and 20 rows of squares, formed by thin black lines on a light gray background. There are no markings or text on the paper.

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Hoskins

Thesis
H81

The identification of certain
clays by differential thermal
analysis

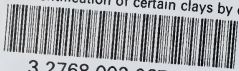
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